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(54) Title: HIGHLY-FILLED POLYMER COMPOSITIONS (57) Abstract Highly-filled polymer compositions retain sufficient base material elasticity as well as the strength required for many critical applications. The composition of the invention are formed of HDPE, LDPE and LLDPE base material, filled with atactic polypropylene-treated extender fillers, and extruded into pipes or sheets. APP-treating permits the compositions of the invention to be filled with up to 80 % by weight of filler, while retaining flexibility. The highly-filled compositions of the invention provide increased durability, an enlarged operating temperature range, improved compatibility with other thermoplastics for welding, coinjection and coextrusion, and are less expensive to produce than prior art filled compositions.		

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HIGHLY-FILLED POLYMER COMPOSITIONS

TECHNICAL FIELD

5 The invention relates generally to extender-filled thermoplastic compositions. More particularly, the invention relates to polyethylene compositions that can be highly loaded with low cost fillers, while maintaining enough flexibility for many critical applications.

DESCRIPTION OF THE PRIOR ART

10 In the last decades, the number of thermoplastic materials have increased not so much through development of new polymers, but through modification of existing ones. By blending two or more different polymers, and/or by adding
15 modifiers, and fillers, properties of polymeric compositions such as strength, resistance to UV and chemical oxidation, shielding, electrical conductivity, and cost can be modified. For example, some inexpensive added extender fillers (hereinafter referred to as "extenders") increase the strength of the polymeric product and decrease its cost. All too often, however, while the targeted
20 properties improve, some other properties deteriorate beyond the level acceptable for the given application.

The importance of fillers in the plastic industry is to some degree reflected by the fact that production of fillers has been growing at a faster pace than that of
25 plastics in general. Inexpensive extenders having microsphere-like particles, such as fly ash, reground post-industrial and post-consumer plastic (hereinafter referred to either as "used plastic" or "recycled plastic") are commonly used as polymer fillers. Extrapolating from the figures of 1967 to 1985 (provided by Kiln and Co.), the current total annual US use of extenders could be above
30 2,000,000 tons. Other sources have higher estimates.

Carlson and Banks, *Particulate Fly Ash Beads*, U.S. Pat. No. 3,830,776 (20 August 1974) discloses a method for separating particulate fractions from fly ash for use as a filler for epoxy. The compositions formed by this method have high
35 crush resistance and strength, but are relatively rigid.

Klingaman and Ehrenreich, *Pyroplastoid Particles, Composition and Method of Production*, U.S. Pat. No. 4,294,750 (13 October 1980) discloses a method for

separating filler particles from coal-burning power plants' fly ash for use in a nylon-based composition. These pyroplastoid particles are ellipsoidal in shape and at least 90 % by weight are less than 25 μ in size.

- 5 In 1986, Electric Power Research Institute (EPRI) in Palo Alto, California, published a study (EPRI CS-4765, Project 2422-11), Evaluation of Plastic Filler Applications for Leached Fly Ash. The study looked into the commercial potentials of acid-leached fly ash from coal-burning power stations. Their conclusion was that the leached fly ash has a potential as filler for polymeric compositions. They also concluded that the higher the ash content in a polypropylene or nylon composition, the more drastically the elasticity of the composition drops. That deficiency explains why such an inexpensive and widely available extender as fly ash is not widely used in polymer industry. Instead, much of the fly ash, a plentiful byproduct of power generation, is currently disposed in landfills at a considerable expense (up to \$50/ton) to the coal-burning power stations.

Ryle et al, *Unstretched Synthetic Papers and Methods of Producing Same*, U.S. Pat. No. 5,308,693 (3 May 1994) discloses a non-stretched synthetic paper having 10 to 25 wt. % diatomaceous earth-filled and HDPE-based compositions. Synthetic paper is increasingly being used in countries where wood is expensive. Since synthetic paper does not produce dust or tear easily, it has additional value for the high speed printing industry. Despite the advantages of synthetic paper, its cost is still too high to compete with wood-pulp paper in countries having abundant wood resources.

To improve the bond between a filler and the rest of the polymer composition, various so-called "coupling agents" are empirically selected, and fillers are treated with them either prior to being mixed into the composition, or during in-line compounding. For example, it is known that treatment of fine-grain fillers with silicone hydrates (S_nH_{2n+2}) maximizes the hydrophobicity and optimizes the electrical properties of filled polymer compositions; it is known that preliminary treatment of a filler with the hydrates of *Si* or *Ti* will improve the impact strength, thermal resistance, water stability, and strain-stress properties of filled compositions.

Atactic polypropylene has been known to increase the levels of carbon black and fire retardants in compositions, Kawai et al., *Electroconductive Resin*

Composition, U.S. Pat. No. 4,425,262 (10 January 1984) and Atwell et al., *Flame Retardant Hot Melt Adhesive Compositions Using Brominated Styrene/Atactic Polypropylene Graft Copolymers*, U.S. Pat. No. 5,041,484 (20 August 1991). Atactic polypropylene has also been used as a thermally-removable binding agent for ceramics, Dolhert, *Clean Burning Green Ceramic Tape Cast System Using Atactic Polypropylene Binder*, U.S. Pat. No. 5,256,609 (26 October 1993). However, these compositions are not suitable for molding into rigid components that maintain some flexibility.

- 10 It has also been known that, on at least on occasion, an atactic polypropylene-treated, extender-filled composition formed with an HDPE base has shown good retention of its elongation. However, this composition didn't provide sufficient strength to be used for pressure pipes or for other critical applications. In addition, this particular composition showed significantly lower productivity
- 15 than compositions of this invention and did not use recycled polymers, all of which is a subject of this invention.

While the extender fillers improve the modulus of elasticity of a composition, they drastically reduce its elongation at its breaking point. For any product

20 which incorporates flexing elements or which has to withstand even occasional surface impacts, such as containers, furniture, instrument housings, automotive oil pans, bumpers and body panels, this reduced elongation is detrimental. Thus, for all practical purposes these filled polymers cannot be effectively used for items requiring stretching or bending properties.

25

Table 1 shows the change of some properties for a selected group of polymer compositions loaded about 40 wt. % with various microspheric fillers.

Polymer & Filler	Amount of Filler wt. %	Impact Energy (Isold with cut) Joule/meter	Modules of Elasticity (bending) MPa	Tensile Yield Limit MPa	Elongation at break %
Polypropylene	-	69	931	23	93 %
Filled Polypropylene					
Talc	40 wt. %	27	2,617	22	8 %
CaCO ₃	40 wt. %	37	1,939	18	12 %
Glass Microsph.	40 wt. %	32	1,497	14	43 %
Cenospheres	40 wt. %	32	1,731	16	33 %
Polyamide 6,6	-	43	2,335	72	58 %
Filled Polyamide 6,6					
Talc	40 wt. %	27	5,265	73	1.6%
CaCO ₃	40 wt. %	32	4,411	75	1.9%
Glass spheres	30 wt. %	32	3,008	56	12 %
Cenospheres	40 wt. %	21	4,227	65	1.9%
Polyvinylchloride	-	758	2,525	51	32 %
Filled Polyvinylchl.					
Talc	40 wt. %	32	5,954	44	1.8%
CaCO ₃	40 wt. %	32	4,609	42	2.3%
Glass Microsph.	40 wt. %	37	3,853	29	30 %
Cenospheres	40 wt. %	32	4,160	27	22 %

Table 1

(The data was published in *Plastics Compound*, 1986, v. 9, no. 7, pp. 12-18, and still reflects the state of the art for microsphere-loaded polymer composition; all filling percentages are given in weight.)

As shown in Table 1, these microspheric fillers improve the modulus of elasticity of a composition, but drastically reduce its elongation at the break. Thus, for all practical purposes, these filled polymers cannot be effectively used for critical items under stretch or bending. For any product which incorporates flexing elements or which has to withstand even occasional surface impacts, such as containers, furniture, instrument housings, automotive oil pans, bumpers and body panels, this kind of shortcoming is detrimental.

It would be an advantage to provide highly-filled polymer compositions that retain a high modulus of elasticity as well as increased elongation. It would be a further advantage if these compositions contain more filler than known in the art. It would be still a further advantage if these compositions contain more recycled polymers than known in the prior art, thus rendering them more environmentally beneficial.

SUMMARY OF THE INVENTION

- 5 This invention relates to extender-filled and atactic polypropylene-treated polymer compositions which, at high levels of loading (30 % by weight and higher), retain sufficient base material elasticity as well as the strength required for many critical applications. The compositions of the invention are formed mostly of HDPE, LDPE and LLDPE, filled with atactic polypropylene-treated fly ash. The base material may also include recycled polymeric materials.
- 10 APP-treating permits the composition of the invention to be filled with up to 80% by weight of filler, while retaining its flexibility. In a preferred embodiment of the invention, the highly-filled composition is extruded into pipes, sheets, construction elements or general purpose, collapsible shipping boxes.
- 15 The compositions of the invention have increased UV and thermal stability, a smaller coefficient of thermal expansion, and higher resistance to chemical substances and sea water than the prior art compositions, while having a higher productivity.
- 20 In alternate, equally preferred embodiments of the invention, polyvinyl chloride (PVC) or polyethylene terephthalate (PET) are filled with atactic polypropylene-treated fly ash at 30 wt. % and higher. In other, equally preferred embodiments of this invention, calcium carbonate is used as an extender.

BRIEF DESCRIPTION OF THE DRAWINGS

- 25 Fig. 1a is a graph showing experimental results for 30 wt. % ash-filled HDPE/LDPE (70/30) and HDPE/LLDPE (70/30) compositions for various APP concentrations;
- 30 Fig. 1b is a graph showing experimental results for 30 wt. % ash-filled HDPE/LDPE (70/30) and HDPE/LLDPE (70/30) compositions for various APP concentrations;
- 35 Fig. 1c is a graph showing experimental results for 30 wt. % ash-filled HDPE/LDPE (70/30) and HDPE/LLDPE (70/30) compositions for various APP concentrations;

Fig. 1d is a graph showing experimental results for 30 wt. % ash-filled HDPE/LDPE (70/30) and HDPE/LLDPE (70/30) compositions for various APP concentrations; and

- 5 Fig. 2 is a graph showing the distribution of the fly ash particles used in the examples of the composition of the invention.

DETAILED DESCRIPTION OF THE INVENTION

- 10 Fly ash is an ample byproduct of the energy generation process. For all practical purposes, fly ash is inexhaustible source as a low cost extender filler for plastic compositions.

15 When pulverized coal is blown into a high temperature furnace and burned, a byproduct of this process melts into hollow particles resembling microspheres (cenospheres). A large percentage of these particles are hollow because the melt settles around rising gas bubbles. These particles are drawn into the exhaust system and, before they can enter into the atmosphere, are collected by various anti-pollution devices, such as cyclones and baghouses. The chemical
20 composition of fly ash depends on the coal which is burned, on the temperature and on other aspects of the burning process. Currently, fly ash has little commercial use. Although some fly ash is used as a filler for concrete, and as an occasional soil additive in agriculture, much of the produced fly ash is disposed in landfills at the expense of the producers.

25 The preferred embodiment of the invention uses atactic polypropylene at-
[CH₂CH(CH₃)-]_n of 0.83 to 0.87 g/cm³ specific weight (hereinafter referred to as APP). APP improves the quality of bond between the filler and the rest of the polymer composition which, in turn, helps provide for even highly filled
30 compositions to retain much of the base material's elongation.

The best amounts of the modifying agent, APP, were evaluated experimentally. In these experiments, two different base materials for compositions were investigated: (a) various blends of HDPE with LDPE, and (b) various blends of
35 HDPE with LLDPE. During these studies, the following relationships were varied and the outcomes compared:

- The weight ratios of HPDE/LDPE, and well as those of HPED/LLDPE, in the base polymer were varied from 70/30 to 90/10;
 - The amount of fly ash in the composition was changed from 30 to 80 wt. % of the entire composition;
 - The amount of the APP was changed from about 0.1 to 15 wt. % of the composition.
- 10 Table 2 contains experimental results for 30 wt. % fly ash-filled HDPE/LDPE (70/30) and HDPE/LLDPE (70/30) compositions for various APP concentrations.

30 wt. % Ash-Filled Composit.		Base Polymer: 70/30 blend of HDPE/LDPE				Base Polymer: 70/30 blend of HDPE/LLDPE			
		Technological Properties		Physical & Mech. Properties		Technological Properties		Physical & Mech. Properties	
		Moment of rotat. (kg m)	Produc- tivity (dg/min)	Tensile Strength (MPa)	Elong. at Yield (%)	Moment of Rotat. (kg m)	Produc- tivity (dg/min)	Tensile Strength (MPa)	Elong. at Yield (%)
No	APP/Ash Ratio (wt. %)								
1	0.2	2.4	7.9	19.2	30	2.3	7.9	19.3	28
2	0.4	2.4	8.0	19.3	60	2.4	7.9	19.1	55
3	0.5	2.3	8.5	24.2	600	2.2	8.4	25.1	620
4	1.0	2.1	9.0	25.4	620	2.1	8.5	25.3	615
5	1.5	2.5	9.2	25.1	650	2.6	9.1	23.8	670
6	1.6	2.4	8.3	19.1	100	2.4	8.2	19.2	100
7	2.0	2.3	8.1	18.4	70	2.3	8.1	18.1	60
8	5.2	2.3	8.1	19.1	50	2.2	8.3	18.9	62

*) The compositions correspond with Examples 1 and 2, respectively.

Table 2

15

In Table 2, the acceptable compositions for the given level of filling are shaded. Figs. 1a - d are graphs of the results listed in Table 2.

20

Table 3 is a table listing the properties of 30 wt. % ash-filled, APP-treated HDPE/LDPE (70/30 wt.) composition, according to the preferred embodiment of the invention.

Property	Typical Value
Density: Reference	1.12 g/cm ³
Nominal	1.05 g/cm ³
Melt flow index (5 kg at 230°C)	0.35 g/10min
Carbon Black Content	2 to 2.5 wt. %
Tensile strength at yield	25.1 MPa (~3,600 PSI)
Strength of weld	25.3 MPa (~3,600 PSI)
Ultimate elongation at yield	650 %
ESCR, F ₅₀	> 200 hr
Hardness	62 Shore D
Charpy Impact Strength	No failure
Creep modules, E ₀	1,100 MPa (~157,000 PSI)
Brittleness temperature	< - 60°C
Linear thermal expansion (Average value for temperature range from 20°C to 90°C)	5 x 10 ⁻⁵ /°C
Thermal conductivity (at 20°C)	0.31 w/m°C
Specific heat	1.79 cal/kg°C
Crystalline melting range	126 - 130°C
Thermal stability Induction time	15 min at 210°C
Vicat softening temperature	126°C

Table 3

- 5 Table 4 is a table listing the properties of 30 wt. % ash-filled HDPE/LDPE (90/10) and HDPE/LLDPE (90/10) compositions for various APP concentrations.

30 wt. % Ash-Filled Composit.		Base Polymer: 90/10 blend of HDPE/LDPE				Base Polymer: 90/10 blend of HDPE/LLDPE			
		Technological Properties		Physical & Mech. Properties		Technological Properties		Physical & Mech. Properties	
No	APP/Ash Ratio (wt. %)	Moment of Rotat. (kg m)	Produc- tivity (dg/min)	Tensile Strength (MPa)	Elong. at Yield (%)	Moment of Rotat. (kg m)	Produc- tivity (dg/min)	Tensile Strength (MPa)	Elong. at Yield (%)
3	0.5	2.5	7.7	21.8	540	1.9	7.4	22.1	546
4	1.0	2.0	8.9	22.9	558	1.8	7.5	23.3	543
5	1.5	2.3	8.3	22.6	585	2.3	8.0	20.9	590

Table 4

10

In Table 4, as it was in Table 2, the acceptable compositions for the given level of filling are shaded.

The above mentioned combinations of HDPE, LDPE (or LLDPE) and of fly ash were blended together with the above described APP in two cyclically operating mixtures. The blending procedure used in the experimental work is described in more detail later. The blends of base materials, filler and APP came out as powders.

Using a laboratory Brabender extruder, the batches of different compositions were extruded into sheets, standard test specimens (double paddles) were cut out of them, and tensile strength at yield and ultimate elongation at yield tested according to ASTM 638. All other tests of technological properties of the composition and the mechanical properties of the test specimens were also conducted according to accepted industry standards.

In order to compare the effect of APP on physical and mechanical parameters of the invented compositions, control samples were made for comparison using prior art coupling agents, such as calcium stearate and vinyltriethoxy silane. All other conditions were kept the same.

The results of the control samples show that, starting above a 10 wt. % level of filling, all the test samples became unstretchable, for all practical purposes. The test samples break before forming a distinctive neck. When the fly ash was treated with APP at certain APP/Ash ratios, the tested samples retained up to 70% or even 90% of the base material's cold stretching ability even at 30-35 wt. % loading.

Another experimentally affirmed conclusion was that, for all practical purposes, the favorable ratio of APP/Ash -- 0.5 to 1.5 wt. % -- does not depend on the ratio of HDPE/LDPE or HDPE/LLDPE in the base material, or on the level of fly ash in the composition.

When using fillers having particles with less distinctly microspheric features, such as calcium carbonate, metal powders, and regrounds of used plastics, it was found that the upper level of APP/Filler ratio can go as high as 10 wt. %. For fillers with high level of absorption for APP, such as some organic fillers (e.g., sawdust), the upper level of APP/Filler can be as high as 15%.

Fly ash-filled and APP-treated composition based of blends of HDPE and its copolymers have a number of properties that are better than those of the base

material alone. For instance, while filled compositions usually lose some of the base material's thermal resistance, the filled compositions treated with APP, especially those filled with fly ash, become more resistant to thermooxidative degradation than the initial base material.

5

In order to test the efficiency of the invention, pipes (OD = 32 mm, h = 2 mm) were extruded from a number of various compositions on a S1.30.25 twin screw extruder. Processing parameters are given in Example 1.

- 10 These pipes were subjected to various tests. The durability of the pipes was tested according to ASTM 4279. Table 5 contains the results of the durability testing of the pipes of Example 1.

No	Composition of Pipe	Tensile Strengths (MPa)	Max. Elongation (%)	Time before failure (in hours)		
				15 MPa T=20°C t=1 hr	4.2 MPa T=80°C t=44 hr	3 MPa T=80°C t=170 hr
1	HDPE	23.0	>600	12.5	satisfied	satisfied
2*)	30 wt. % Ash, HDPE/LDPE (70/30), APP/Ash Ratio 1 wt. %	25.1	650	2.5	> 44	> 1,000
3*)	30 wt. % Ash, HDPE/LLDPE (70/30), APP/Ash Ratio 1 wt. %	24.7	800	4	> 44	> 1,000

*) These pipes correspond with Examples 1 and 2, respectively.

15

Table 5

- The requirements of ASTM 4279 are given in the shaded part of Table 5. As the results in Table 5 show, the pipes passed the tests. These 32 mm x 2 mm pipes can be used for 0.25 MPa (36 PSI) pressure. For higher pressures, the pipes should have correspondingly larger wall thickness. The high results of the 3 MPa, 80°C test (> 1,000 hours) let us to believe that these pipes made of APP-treated fly ash-filled compositions can be used for hot water supply lines.

- 25 A 10% to 30% productivity increase was expected when switching from extruding HDPE pipes to those made of the fly ash-filled, APP-treated, HDPE/LDPE- and HDPE/LLDPE-based compositions. However, in comparison

with HDPE, the productivity of S1.30.25 twin screw extruder doubled when working with the invented compositions. Nearly the same increase in productivity was observed on Busano twin screw sheet extruder and American Barmag Corp.'s blow extruder.

5

Before describing the specifics of various examples of different nature, here is what was the same for many of them. Here are the properties of the HDPE, LDPE, LLDPE, fly ash, APP, and the blending procedure which were used in the examples when such material or blending procedure were specified:

10

Property	HDPE	LDPE	LLDPE
Density	0.96 g/cm ³	0.93 g/cm ³	0.92 g/cm ³
Melt flow index (5 kg, 230 °C)	0.4-1.0 g/10min	0.55 g/10min	0.75 g/10min
Tensile strength at yield	28 MPa	14 MPa	17 MPa
Ultimate elongation at yield	1,000 %	-	-
Flex modules		210 MPa	210 MPa

Table 6

The fly ash used in the experimental work had the following properties:

15

Specific density 1.95 g/cm³ or less;
 Bulk density 0.90 g/cm³;
 Specific surface 2.5 to 3 m²/g;
 Less than 0.5 % of weight loss after prolonged heating at 200°C
 (DTA thermogravimetry);
 Distribution of particles is characterized in Fig. 2.

20

The curve was obtained using a device based on Coulter Counter measuring technique. This distribution curve shows that the particles of the fly ash used had the mean about 12 mm, 85% of particles were less than 20 mm, with as little as possible of dust-like fractions (1 mm and less).

25

The atactic polypropylene used in the experimental work had the following physical characteristics:

- | | | |
|---|-------------------------------|--------------------------------|
| 5 | Specific weight | 0.83 to 0.87 g/cm ³ |
| | Vapor pressure | 10 mm of Hg at 350 °F |
| | Ring and ball softening point | 230 °F |
| | Flash point | > 300 °F |
| | Fire point | > 350 °F |
- 10 The polymeric components, fillers and APP were blended in *M-2400/K* two-step mixer (300-330 kg/hour capacity, made by *MTI*, Germany); hot mixing for 20 to 25 minutes at 90°C, and then cold mixing for 10 to 20 minutes at 40°C. The primary purpose of the second stage was cooling.
- 15 The following Examples are included to illustrate the actual invention; but they should not limit the scope of the invention or Claims. All parts and percentages are by weight.

EXAMPLE 1

20

Extruded 3.2 mm x 2 mm Pressure Pipe from 30 wt. % Ash-Filled Composition Based on 70/30 (wt. ratio) HDPE/LDPE.

Composition:

25

HDPE	70	wt.
LDPE	30	wt.
Fly ash	42.2	wt.
APP	0.42	wt.

30

Melt flow index of the composition (5 kg, 230°C) was 0.42 g/10 min.

The technological parameters of extrusion were as follows:

35	Cylinder	180°C,	185°C,	190°C,	195°C
	Head	200°C			
	Die	205°C			
	Melt Temp.	200 - 210°C			

- (d) Solutions of diluted organic acids,
- (e) Organic acids insoluble in water,
- (f) Solutions of mineral salts,
- (g) Alkali solutions,
- 5 (h) Solutions of oxidants,
- (i) Mineral oils,
- (j) Aliphatic solvents
- (k) Aromatic solvents,
- (l) Halogens-containing aliphatic solvents.

10

The assessments were based on the resistance of HDPE to mild solutions of mineral acids at normal temperature, to which "5" was assigned: HDPE has high resistance under those conditions. If a given material in a given environment and temperature lost the same or smaller percentage of its original weight as did HDPE in mild solutions of mineral acids at normal temperatures, "5" was assigned to that material in the given conditions. "4" was assigned to a satisfactory resistance of a coating material. "3" meant that the resistance was not always satisfactory. "2" and "1" indicated that the resistance of a coating material was unsatisfactory and therefore the material is not recommended for that particular circumstance.

20

Assessment of the resistance of each HDPE pipe at normal temperature was written first, and after the slash sign the same for hot temperature.

- 25 The outcome of these assessment tests is given in Table 9. The assessment of the resistance of each fly ash-filled, 70/30 HDPE/LDPE-based piece of pipe at normal temperature is listed first, with the hot temperature figure listed next.

Material of Pipe	Assessments of Materials in Given Environments											
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)
HDPE	5/5	5/5	5/3	5/4	3/2	5/5	5/5	4/2	4/2	3/2	1/1	1/1
30 wt. % ash-filled, 70/30 wt. ratio HDPE/LDPE	5/5	5/5	5/4	5/5	4/4	5/5	5/5	4/3	4/4	4/4	2/3	2/3

Table 9

In the environments marked (k) and (l), the 30 wt. % ash-filled, 70/30 wt. ratio HDPE/LDPE composition behaved even better at hot temperatures than it did at normal temperatures.

- 5 The pieces of pipes were tested for thermooxidation, and the results are contained in Table 10.

Material of Pipe	Inductive Period (in minutes) (Tested at 200 mm Hg pressure and 140°C)
HDPE	105 min
30 wt. % ash-filled, 70/30 (wt. ratio) HDPE/LDPE-based composition	150 min

Table 10

- 10 The thermooxidation tests showed that under the conditions specified in Table 10 the invented composition has almost 50% higher resistance to thermal oxidation than HDPE.

EXAMPLE 2

15

Extruded 3.2 mm x 2 mm Pressure Pipe from 30 wt. % Ash-Filled Composition Based on 70/30 (wt. ratio) HDPE/LLDPE.

Composition:

20

HDPE	70	wt.
LLDPE	30	wt.
Fly ash	42.2	wt.
APP	0.42	wt.

25

The only difference with Example 1 was that instead of LDPE LLDPE was used in the base material.

The pipe had excellent surface and the following properties:

30

Ultimate elongation	e = 800%	
Tensile strength at yield	S = 24.7 MPa	(~ 3,550 PSI)
Strength of weld:	S _w = 24.5 MPa	(~ 3,500 PSI).

The pipe easily passed the durability tests (the test results are given in Table 5, line 3) usually applied for pipes designed for 0.25 MPa (36 PSI) pressure.

5 EXAMPLE 3

Stretch-Oriented Specimen made from 30 wt. % Ash-Filled Composition Based on 70/30 (wt. ratio) HDPE/LLDPE.

- 10 The same composition as in Example 2 was prepared and extruded into a narrow sheet. From this narrow sheet, standard double-bell test specimens were stamped out and tested on Instron test equipment. The speed of deformation was 50 mm/min. Under such stretch, the test specimens developed well observed necks: the maximum coefficient of cold stretch exceeded 6
15 before the specimens broke.

EXAMPLE 4

- Solar Collectors from a Blow Extruded Sleeve, made from 40 wt. % Ash-Filled
20 Composition Based on 70/30 (wt. ratio) HDPE/LLDPE.

Composition:

	HDPE	70	wt.
25	LLDPE	30	wt.
	Fly ash	66	wt.
	APP	0.7	wt.

- A 500 mm diameter and 300 μ m wall thickness sleeve was produced on a blow
30 extruder. The sleeve had the following properties:

	Melt flow rate (5 kg, 230°C)	0.35 g/10min.
	Ultimate elongation in the direction of extrusion	$e_1 = 400\%$
35	Ultimate elongation in the direction perpendicular to extrusion	$e_2 = 500\%$
	Tensile strength at yield in the direction of extrusion	$S_1 = 20.7 \text{ MPa}$ (~ 2,900 PSI)

Tensile strength at yield in the direction perpendicular
to extrusion

$$S_2 = 15.6 \text{ MPa} \quad (\sim 2,200 \text{ PSI})$$

Strength of punctuation

$$S_p = 34.0 \text{ MPa} \quad (\sim 4,760 \text{ PSI})$$

Coefficient of thermal

5 conductivity of the sheet $k = 0.002 \text{ cal cm}/(^{\circ}\text{C cm sec})$

10 The sleeve was cut into meter-long pieces. Each piece was thermo-welded in such a way that it formed a flexible, waterbed mattress-like solar collector, having 12 passages for heated water, an incoming manifold and an outgoing manifold. These solar collectors were tested for three years in a region which had monthly average solar radiation of approximately 36 MJ/m^2 . On a sunny day, this less than 0.7 m^2 solar collector, when in horizontal position and uncovered, heated 45 liters of water hourly from 20°C to 45°C .

15 EXAMPLE 5

Extruded Sheets from 50 wt. % Ash-Filled HDPE/LDPE and HDPE/LLDPE.

20 150 mm wide and 2 mm thick sheets were extruded on Brabender laboratory extruder from two different compositions and tested. The compositions and the test results are listed in Table 7.

No	Composition of sheet (wt.)	Tensile Strength s (MPa)	Max. Elongat. e (%)
1	HDPE - 70, LDPE - 30, ASH - 99, APP - 1	24.1	80
2	HDPE - 70, LLDPE - 30, ASH - 99, APP - 1	26.2	60

Table 7

25 The sheets also had excellent surface, strong weld, and improved rheology leading to higher productivity than extruding the same sheet from unfilled HDPE.

EXAMPLE 6

Filled HDPE as Conductor.

5 **Composition:**

	HDPE	70 wt.
	LLDPE	30 wt.
10	Ni powder (25 μ m average particle size)	147 wt.
	APP	3 wt.

A 300 mm wide and 500 μ m thick sheet was extruded and tested:

15	Density	$r = 1.7 \text{ g/cm}^3$	(~106 lb/ft ³)
	Ultimate elongation at yield	$e = 200 \%$	
	Tensile strength at yield	$S = 18 \text{ MPa}$	(~ 2,550 PSI)
	Coef. of thermal conductivity	$k = 0.005 \text{ cal cm/}^\circ\text{C cm sec}$	
20	Coef. of electrical volume resistivity	$r = 2 \times 10^3 \Omega \text{ cm}$	

This composition can be used for products which should not collect static
electricity, such as conveyor belts and various ventilation pipes in mines and
25 chemical plants, and radiators for automobiles.

EXAMPLE 7

Filled HDPE/LLDPE as Noise Insulator.

5 Composition:

	HDPE	70	wt.	
	LLDPE	30	wt.	
	Fly ash	20	wt.	
10	APP	0.2	wt.	
	Polyurethane foam	80	wt.	(polyurethane foam was recaptured from waste stream)

- 15 A 300 mm wide and 500 μ m thick sheet was extruded and tested. Its dielectric conductivity was 1.9, and the tangent of dielectric losses $\text{tg}10^6$ was 0.018, and $\text{tg}10^3$ was 0.03.

EXAMPLE 8

20

Pipes for Being Laid into Concrete.

The following composition was prepared:

25	HDPE	10	wt.	
	LDPE	10	wt.	
	HPDE (recycled)	50	wt.	(was recaptured from waste stream as milk and water bottles)
	LDPE (recycled)	30	wt.	(was recaptured from waste stream as bags)
30	Fly ash	80	wt.	
	APP	1.2	wt.	

- 35 The composition was extruded into 50 mm x 4 mm pipe. The pipe was tested for its maximum deformation under a load of 1,000 Newton acting perpendicular to its wall; the surface of contact was 25 cm^2 . That load caused less than a 10% change in diameter. Such a pipe can be laid into concrete.

EXAMPLE 9

Irrigation Hoses.

- 5 The same composition as in Example 4 was prepared, and two different sizes of hoses were extruded from this composition:

OD = 100 mm, wall thickness = 200 μ m, and

OD = 300 mm, wall thickness = 300 μ m.

10

These hoses were tested for durability using standard procedures; expected life of these hoses was found to be at least 5 years.

EXAMPLE 10

15

Composition for Cast Molding Pencils

Composition:

20	Polypropylene	68 wt.
	Sawdust	18 wt.
	CaCO ₂	7 wt.
	APP	7 wt.

- 25 Then the standard test specimens (double paddle) were cast molded and tested. The melt index (2.16 kg, 230°C) was 13 g/10 min. Such pencils are easier to sharpen than wooden pencils, and can be sharpened either with a pocket knife or with all standard pencil sharpening devices.

EXAMPLE 11

Films for Soil Cover.

5 **Composition:**

	HDPE (recycled)	38 wt.
	LDPE (recycled)	17 wt.
	Bitumen	20 wt.
10	Fly Ash	25 wt.
	APP	5 wt.

A 100 μ m film was extruded from it.

15 **EXAMPLE 12**

Composition for Rotational Casting.

Composition:

20	HDPE	32 wt.
	LDPE	32 wt.
	Polyurethane foam	20 wt.
	Bitumen	5 wt.
25	Fly ash	10 wt.
	APP	1 wt.

Standard test specimens were cast molded and tested:

30	Ultimate elongation at yield	e = 100 %
	Tensile strength at yield	s = 19 MPa (~2,700 PSI)

EXAMPLE 13

Extruded Sheets Using Coextrusion (when at least one layer has with recycled plastic in it).

5

The following two compositions were prepared for a three-layer coextruded sheet A-B-A. Composition A consisted of fresh HDPE and fresh LDPE:

	HDPE	70 wt.
10	LDPE	30 wt.

Composition B:

	Recycled HDPE	35	wt.
15	Recycled LDPE	15	wt.
	Fly ash	49.2	wt.
	APP	0.8	wt.

20 A 1.5 mm thick and 1,500 mm wide sheet was coextruded from these two compositions. Two outside layers of the sheet were coextruded from composition A, and the middle layer from composition B. The outside and inside layers were both 50 μ m thick, the middle layer was 1.4 mm thick. This sheet had excellent resistance to the elements.

25 EXAMPLE 14

Extruded Sheets Using Coextrusion (when at least one layer has with recycled plastic in it).

30 The outside layers were the same as Example 13, but a different composition B was used for the middle layer. Recycled polyethylene therephthalate (PET) was used instead of HDPE/LDPE, and the proportions of the composition were different:

35	Recycled PET	80	wt.
	Fly ash	20	wt.
	APP	1.5	wt.

Then, as in Example 13, a 1.5 mm thick and 1,500 mm wide sheet was coextruded from these two compositions. Two outside layers of the sheet were coextruded from composition A, and the middle layer from composition B. The outside and inside layers were both 50 μ m thick, the middle layer was 1.4 mm thick. This sheet had also excellent resistance to the elements.

EXAMPLE 15

Antistatic Composition for Wires and Cables.

10

The following composition was prepared:

	HDPE	90 wt.
	LDPE	10 wt.
15	Carbon black	60 wt.
	Fly ash	37 wt.
	APP	3 wt.

Using Brabender with a centering crosshead, the composition was extruder to insulate about 1 mm² copper wire; the insulation was about 300 μ m thick. The insulation displayed good adhesion to the wire and good resistance to the elements.

EXAMPLE 16

25

Composition for Synthetic Paper;
Compatibility of Usually Incompatible Compositions.

Composition:

30

	PVC	70 wt.
	Polyurethane	47 wt.
	HDPE	30 wt.
	CaCO ₃	50 wt.
35	APP	3 wt.

A narrow strip was extruded from it on *Brabender*. This strip demonstrated excellent adhesion for inks and dyes; no molecular reorientation (which is usually done by stretching) was needed.

- 5 Then the strip was welded with a strip made of HDPE, and another strip made of PVC. The welds were excellent.

The same results were obtained when, instead of chalk, the same weight of fly ash was added into the composition:

10

Polyvinyl chloride	70 wt.
Polyurethane	47 wt.
HDPE	30 wt.
Fly ash	50 wt.
APP	5 wt.

15

Both of these highly filled compositions can also be used in coextrusion of PVC-composition-HDPE (or its copolymers).

20 **EXAMPLE 17**

Anticorrosion Coatings for Metal Pipes.

Composition:

25

HDPE	90 wt.
LDPE	10 wt.
Fly ash	42.2 wt.
APP	0.42 wt.

30

The composition was used for anti-corrosion coating of 100 mm metal pipes. The composition was loaded into a hopper of plasma deposition equipment and deposited as a 250 μm to 300 μm thick coating. During the plasma-deposition, the surface temperature of the pipes was kept over 150°C;

35

The equipment used for plasma deposition was that widely applied in anti-corrosive coating of pipe.

Accordingly, the invention should only be limited by the Claims included below.

CLAIMS

1. A highly-filled polymer composition, comprising:
a base polymer consisting of blend of HDPE and LDPE in ratio from
5 70/30 to 90/10 by weight;
fly ash as a filler in amount of 30% to 80% of the base polymer (by
weight); and
atactic polypropylene of 0.83 to 0.87 g/cm³ specific weight in amount of
0.5% to 1.5% from the weight of fly ash.
10
2. The highly filled composition of Claim 1, wherein said base material is
substituted either partially or fully by the same blend of reground used plastic
materials, and the said amount of atactic polypropylene is increased by 1% to
3% of the weight of the substituted used plastic;
15
3. The highly filled composition of Claim 1, wherein said base material is
substituted either partially or fully by reground used HDPE, and the amount of
said atactic polypropylene is increased by 1% to 3% of the weight of the
substituted used plastic;
20
4. A highly-filled polymer composition, comprising:
a base polymer consisting of blend of HDPE and LDPE in ratio from
70/30 to 90/10 by weight;
calcium carbonate as a filler in amount of 30% to 80% of the base
25 polymer (by weight); and
atactic polypropylene of 0.83 to 0.87 g/cm³ specific weight in amount of
2% to 10% from the weight of calcium carbonate.
5. The highly filled composition of Claim 4, wherein said base material is
30 substituted either partially or fully by the same blend of reground used plastic
materials, and the amount of said atactic polypropylene is increased by 1% to
3% of the weight of the substituted used plastic;
6. The highly filled composition of Claim 4, wherein said base material is
35 substituted either partially or fully by reground used HDPE, and the amount of
said atactic polypropylene is increased by 1% to 3% of the weight of the
substituted used HDPE;

7. A highly-filled polymer composition, comprising:
a base polymer consisting of blend of HDPE and LLDPE in ratio from 70/30 to 90/10 by weight;
fly ash as a filler in amount of 30% to 80% of the base polymer (by weight); and
5 atactic polypropylene of 0.83 to 0.87 g/cm³ specific weight in amount of 0.5% to 1.5% from the weight of fly ash.
8. The highly filled composition of Claim 7, wherein said base material is substituted either partially or fully by the same blend of reground used plastic materials, and the amount of said atactic polypropylene is increased by 1% to 3% of the weight of the substituted used plastic;
9. The highly filled composition of Claim 7, wherein said base material is substituted either partially or fully by reground used HDPE, and the amount of said atactic polypropylene is increased by 1% to 3% of the weight of the substituted used plastic;
10. A highly-filled polymer composition, comprising:
20 a base polymer consisting of blend of HDPE and LLDPE in ratio from 70/30 to 90/10 by weight;
calcium carbonate as a filler in amount of 30% to 80% of the base polymer (by weight); and
atactic polypropylene of 0.83 to 0.87 g/cm³ specific weight in amount of
25 2% to 10% from the weight of calcium carbonate.
11. The highly filled composition of Claim 10, wherein said base material is substituted either partially or fully by the same blend of reground used plastic materials, and the amount of said atactic polypropylene is increased by 1% to 30 3% of the weight of the substituted used plastic;
12. The highly filled composition of Claim 10, wherein said base material is substituted either partially or fully by reground used HDPE, and the amount of said atactic polypropylene is increased by 1% to 3% of the weight of the substituted used HDPE;
35

13. A highly-filled polymer composition, comprising:
PET as a base polymer;
fly ash in amount of 30% to 80% of the base polymer (by weight); and
atactic polypropylene of 0.83 to 0.87 g/cm³ specific weight in amount of
5 0.5% to 1.5% from the weight of fly ash.
14. The highly filled composition of Claim 13, wherein said base material is
substituted either partially or fully by reground used PET, and the amount of said
atactic polypropylene is increased by 1% to 3% of the weight of the substituted
10 used PET;
15. A highly-filled polymer composition, comprising:
PET as a base polymer;
calcium carbonate as a filler in amount of 30% to 80% of the base
15 polymer (by weight); and
atactic polypropylene of 0.83 to 0.87 g/cm³ specific weight in amount of
2% to 10% from the weight of calcium carbonate.
16. The highly filled composition of Claim 15, wherein said base material is
20 substituted either partially or fully by reground used PET, and the amount of said
atactic polypropylene is increased by 1% to 3% of the weight of the substituted
used PET;
17. A highly-filled polymer composition, comprising:
25 PVC as a base polymer;
fly ash in amount of 30% to 80% of the base polymer (by weight); and
atactic polypropylene of 0.83 to 0.87 g/cm³ specific weight in amount of
0.5% to 1.5% from the weight of fly ash.
18. The highly filled composition of Claim 17, wherein said base material is
30 substituted either partially or fully by reground used PVC, and the amount of
said atactic polypropylene is increased by 1% to 3% of the weight of the
substituted used PVC;
19. A highly-filled polymer composition, comprising:
35 PVC as a base polymer;
calcium carbonate as a filler in amount of 30% to 80% of the base
polymer (by weight); and

atactic polypropylene of 0.83 to 0.87 g/cm³ specific weight in amount of 2% to 10% from the weight of calcium carbonate.

20. The highly filled composition of Claim 19, wherein said base material is substituted either partially or fully by reground used PVC; and the amount of said atactic polypropylene is increased by 1% to 3% of the weight of the substituted used PVC;
21. The use of highly fly ash-filled and atactic polypropylene-treated compositions for making plastic substitutes for wood products, such as plywood and particle board, elements of furniture, load-carrying beams, rafters, subfloors, subroofs, roof elements, siding for buildings, piles, posts, various containers for storing and shipping various products.
22. The use of highly fly ash- or calcium carbonate-filled and polypropylene-treated compositions for making synthetic paper and various products therefrom.

1/3

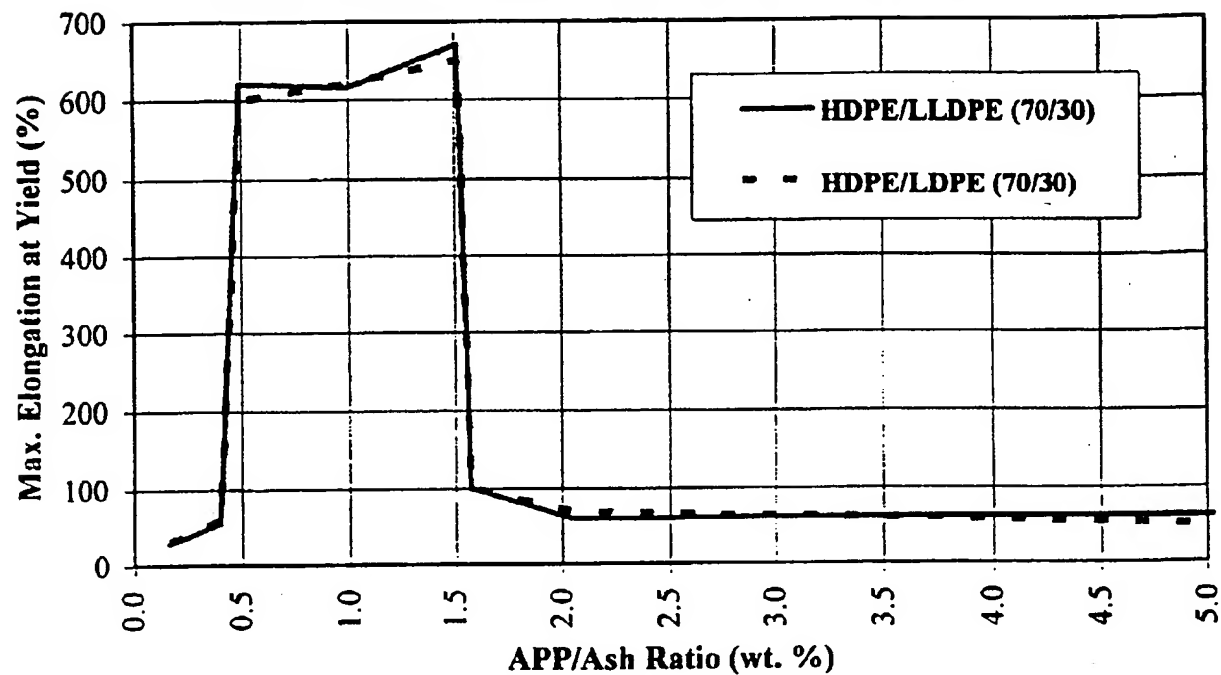
Max. Elongation at Yield vs. APP/Ash Ratio

Fig. 1a

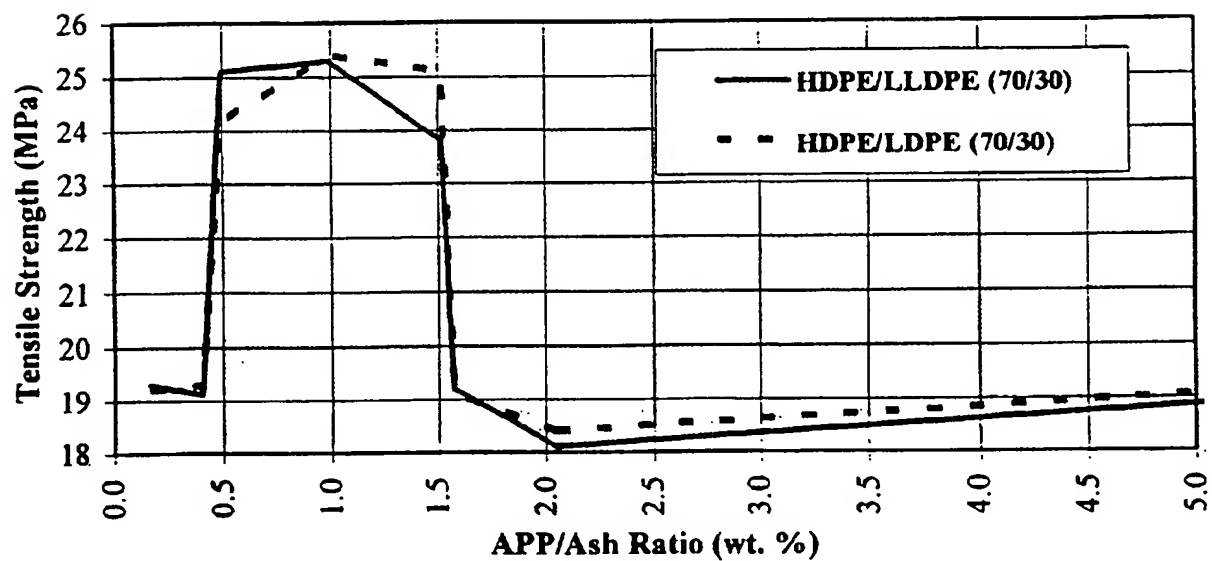
Tensile Strength vs. APP/Ash Ratio

Fig. 1b

2/3

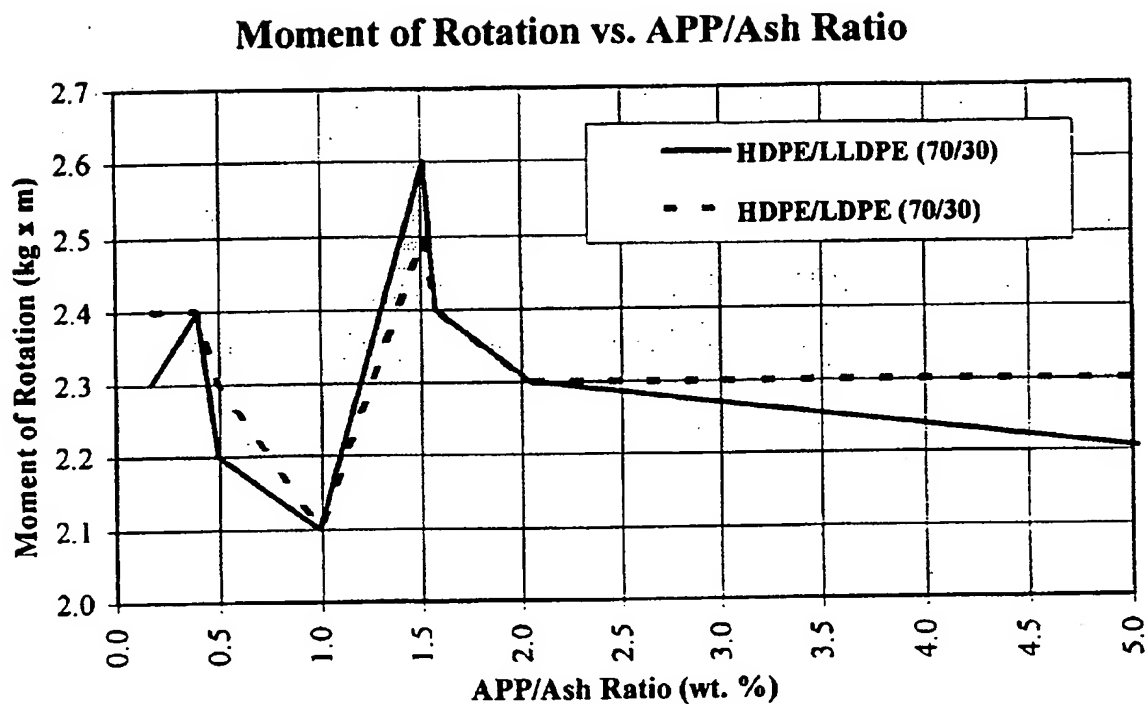


Fig. 1c

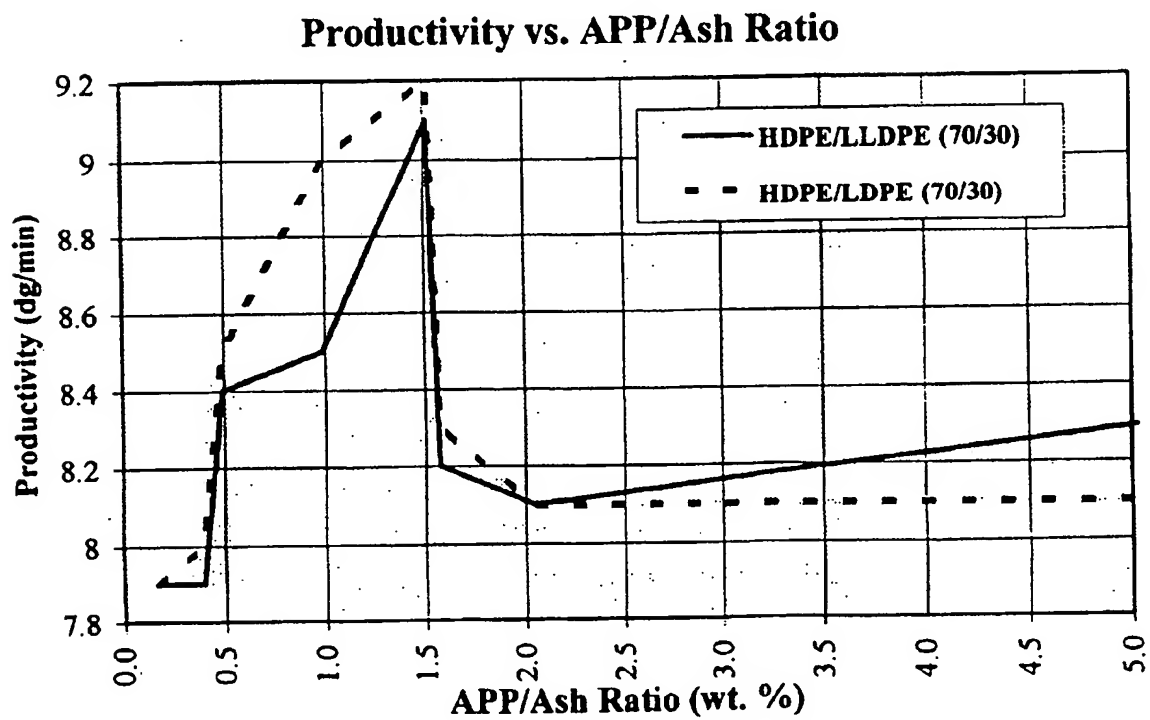
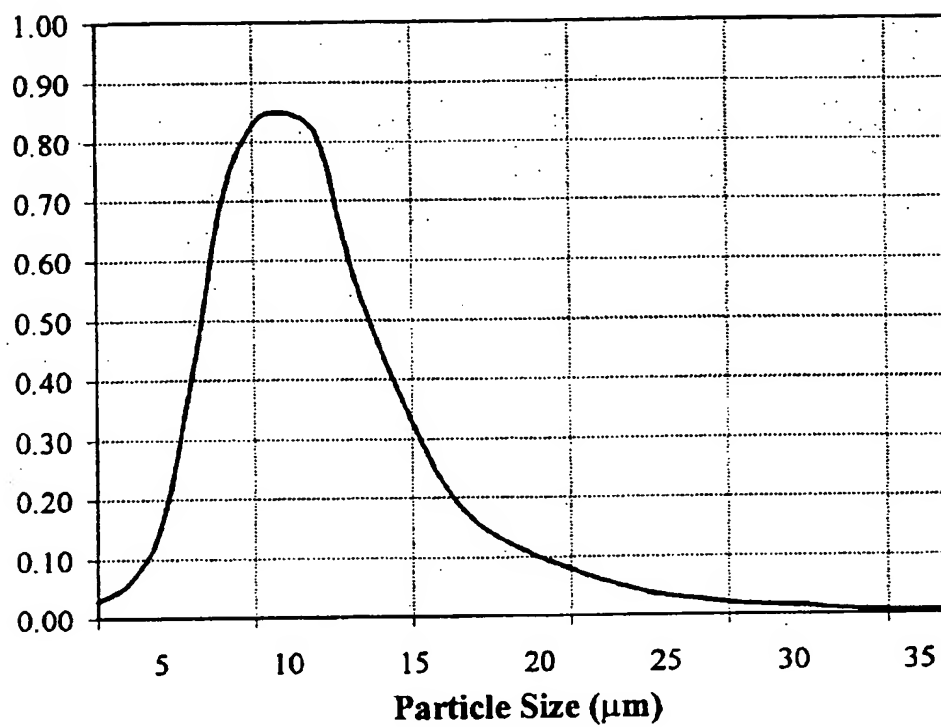


Fig. 1d

Distribution of Ash Particles

**Fig. 2**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/15018

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08J 5/10, 9/32; C08K 3/04, 3/26, 9/00; C08L 23/06
US CL : 523/215, 218; 524/495, 496, 425

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/215, 218; 524/495, 496, 425

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,030,662 (BANERJIE) 09 July 1991, entire document.	1-22
Y	SU, A, 1194008 (RESEARCH AND PRODUCTION ORGANIZATION "UZYBYPLASTIK") 17 May 1984, entire document.	1-22

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

A	document defining the general state of the art which is not considered to be of particular relevance	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E	earlier document published on or after the international filing date	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O	document referring to an oral disclosure, use, exhibition or other means	*Z*	document member of the same patent family
P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

09 DECEMBER 1996

Date of mailing of the international search report

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Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

U.K. RAJGURU

Telephone No. (703) 308-2351